Thermodynamic optimization and calculation of the YCl₃–ACl (A=Li, Na, K, Rb, Cs) phase diagrams

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ABSTRACT

The binary phase diagrams of the YCl₃–ACl (A=Li, Na, K, Rb, Cs) systems were studied using the CALPHAD technique and nonlinear mathematical method. The new modified quasi-chemical model in the pair-approximation for short-range ordering was applied to describe the Gibbs energies of the liquid phase in these systems. And the paper created the Artificial Neural Networks (ANN) model to study the interaction coefficients of two ending compounds composing the binary systems which are important for thermodynamic study of multi-elements system. Based on measured phase equilibrium data, a set of thermodynamic functions has been optimized and calculated. The effects of ionic radius, electronegativity and mole fraction of YCl₃ on interaction coefficients were investigated in more detail.

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1. Introduction

Entering the 21st century the rare earths play a very important role in modern materials [1]. The electrolysis of molten salt of the rare earths has been widely used for production of rare earth metals and their alloys. Here is a work of our series studies using the CALPHAD technology to examine and optimize the experimental phase diagram then obtain a number of thermodynamical parameters for the binary systems.

To continue our previous work [2–7], the thermodynamic optimizations and calculation of the YCl₃–ACl (A=Li, Na, K, Rb, Cs) systems are carried out in this study. This work investigated the changing law of interaction coefficient (mixing enthalpy) in micro-properties of elements composing the binary systems for the first time; meanwhile the modified quasi-chemical model in the pair-approximation for the short-range ordering was used to describe the liquid phase's thermodynamic properties (MQCs in short). Through the measured data by XRD (X-ray diffraction), DTA (differential thermal analysis) and experimental integral properties, the systems' phase diagrams were optimized. The results showed that the optimized parameters and experimental data are thermodynamically self-consistent.

2. Thermodynamical model

Pelton and Blander [8–10] and Blander et al. [11] proposed a short-range ordering model, a more universal model, based on the quasichemical theory of Guggenheim [12] and Guggenheim and Fowler [13] to describe and optimize thermodynamic properties of binary system with the strong interaction between two side compounds. Instead of the real components A and B in the system, the first-nearest-neighbor pairs A–A, B–B, A–B were used in this model.

$$(A-A)_{\text{pair}} + (B-B)_{\text{pair}} = 2(A-B)_{\text{pair}} \tag{1}$$

$$Z_A n_A = 2n_{AA} + n_{AB} \tag{2}$$

$$Z_B n_B = 2n_{BB} + n_{AB} \tag{3}$$

where, n_A and n_B are the number of moles of A and B, n_{ij} is the number of moles of (i–j) pairs. The coordination numbers of A and B are the Z_A and Z_B.

$$\frac{1}{Z_A} = \frac{1}{2n_{AA} + n_{AB}} \left(\frac{2n_{AA}}{Z_{AA}} + \frac{n_{AB}}{Z_{AB}} \right) \tag{4}$$

$$\frac{1}{Z_B} = \frac{1}{2n_{AA} + n_{AB}} \left(\frac{2n_{BB}}{Z_{BB}} + \frac{n_{AB}}{Z_{BA}} \right) \tag{5}$$

The Z_{ij} is the coordination number of i–j pair.

In Eqs. (4) and (5), Z_{AA} and Z_{BB} are the coordination numbers of pure component A and pure component B.

The pair fraction X_{ij} is defined as

$$X_{ij} = \frac{n_{ij}}{(n_{AA} + n_{BB} + n_{AB})} \tag{6}$$

Aslo, the mole fractions X_A and X_B are defined as

$$X_A = \frac{n_A}{(n_A + n_B)} = 1 - X_B \tag{7}$$

And the coordination-equivalent fractions Y_A and Y_B are defined as follows:

$$Y_A = Z_A n_A / (Z_A X_A + Z_B n_B) = Z_A X_A / (Z_A X_A + Z_B X_B) = 1 - Y_B \tag{8}$$

By substituting Eqs. (2) and (3) into Eqs. (6) and (8), some equations are obtained as follows:

$$Y_A = X_{AA} + \frac{X_{AB}}{2} \tag{9}$$

$$Y_B = X_{BB} + \frac{X_{AB}}{2} \tag{10}$$

Eq. (11) shows the mole Gibbs energy of solutions

$$G = (n_A g_A^0 + n_B g_B^0) - T\Delta S^{config} + n_{AB}/2 \Delta g_{AB} \tag{11}$$

where g_A^0 and g_B^0 mean the pure component's mole Gibbs energy, and ΔS^{config} is the configurational entropy of mixing given by randomly distributing the $(A–A)$, $(B–B)$ and $(A–B)$ pairs.

$$\Delta S^{config} = -R(n_A \ln X_A + n_B \ln X_B)$$
$$- R\left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_L Y_B}\right) \tag{12}$$

The molar pair Gibbs energy of $i–j$ pairs, i.e., g_{AA}^0, g_{BB}^0, and g_{AB}^0 are defined according to the following expressions:

$$g_{AA}^0 = \frac{2g_A^0}{Z_{AA}^A}, \; g_{BB}^0 = \frac{2g_B^0}{Z_{BB}^B} \tag{13}$$

$$g_{AB}^0 = \Delta g_{AB}^0 + g_{AA}^0 \frac{Z_{AA}^A}{Z_{AB}^A} + g_{BB}^0 \frac{Z_{BB}^B}{Z_{BA}^B} = \Delta g_{AB}^0 + \left(\frac{2g_A^0}{Z_{AB}^A} + \frac{2g_B^0}{Z_{BA}^B}\right) \tag{14}$$

The Gibbs energy of $A–B$ system is given as follow:

$$G = (n_A g_A^0 + n_B g_B^0) + RT(n_A \ln X_A + n_B \ln X_B)$$
$$+ RT\left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B}\right) + \frac{n_{AB}}{2} \Delta g_{AB} \tag{15}$$

In Eq. (15), Δg_{AB} is the molar energy of $A–B$ pairs, also it is a function of the mole fractions of $i–j$ pairs, and it can be expressed as follows:

$$\Delta g_{AB} = \Delta g_{AB}^0 + \sum g_{AB}^i X_{AA}^i + \sum g_{AB}^j X_{BB}^j \tag{16}$$

or

$$\Delta g_{AB} = \Delta g_{AB}^0 + \sum g_{AB}^{ij} X_{AA}^i X_{BB}^j \tag{17}$$

In Eqs. (16) and (17), $i + j \geq 1$. If $i = 0$ or $j = 0$, it means the mixing influence of the system was not considered.

3. Study of interaction coefficient

3.1. Nonlinear model of interaction coefficient

The interaction coefficient as a macro-property is important for thermodynamic study of multi-elements system. The micro-structures of the matter including spacial and electrical properties of elements determine the macro-properties of the matter. To study these binary systems in more detail, the interaction coefficients representing mixing enthalpy usually considered in different thermodynamic models such as model of ideal solution, regular solution and quasi-chemical solution, were tried to study at microstructure angle by building the micro–macro model.

The interaction coefficients by thermodynamic models are usually hard to get good agreements with experimental data. Even the latest model like the quasi-chemical model shows not so good results (see Fig. 6).

Artificial Neural Networks (ANN) as a powerful nonlinear technology was chosen to use in the first time in this study, because of the complexity of relations among the microstructures and the interaction coefficients. At present the same study was not found in published paper. The three-layer back propagation of ANN was considered in building the model. The 3-3-1 topologic structure was shown below. We call this way as Interaction Coefficient Model by Neural Networks (ICN[2] in short). According to the 49 sets of experimental data [14], the leave-three-out principle was obeyed in the study. It means when data was trained in 3-3-1 topologic structure networks the 46 training sets of data were chosen from 49 randomly. These 46 sets of data were also used to test. The left 3 sets of data were used to validate (Fig. 1).
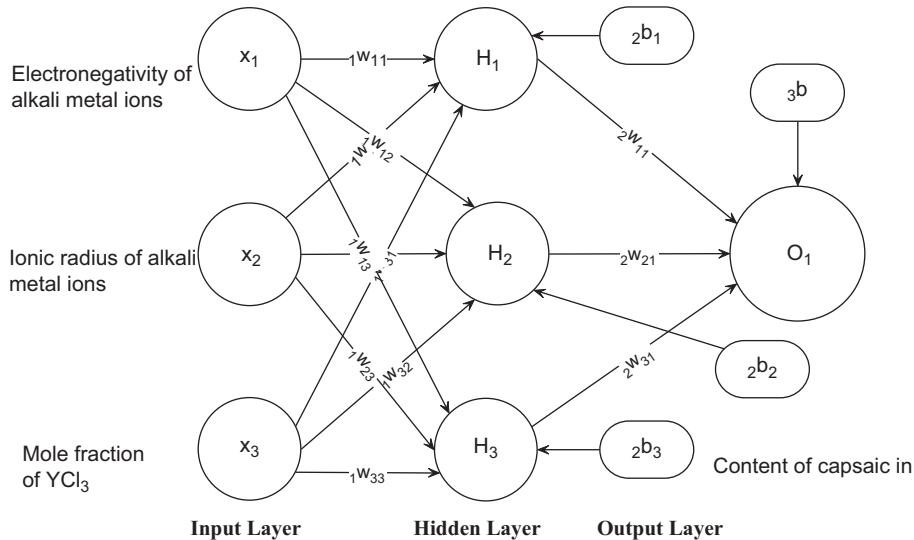

Fig. 1. Topologic structure of 3-3-1 networks.